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# Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications

Ken Caldeira

DOE Center for Research on Ocean Carbon Sequestration, Lawrence Livermore National Laboratory, Livermore, California USA

Greg H. Rau

Institute of Marine Sciences, University of California, Santa Cruz, California USA

**Abstract.** Various methods have been proposed for mitigating release of anthropogenic $CO_2$ to the atmosphere, including deep-sea injection of $CO_2$ captured from fossil-fuel fired power plants. Here, we use a schematic model of ocean chemistry and transport to analyze the geochemical consequences of a new method for separating carbon dioxide from a waste gas stream and sequestering it in the ocean. This method involves reacting $CO_2$-rich power-plant gases with seawater to produce a carbonic acid solution which in turn is reacted on site with carbonate mineral (e.g., limestone) to form $Ca^{2+}$ and bicarbonate in solution, which can then be released and diluted in the ocean. Such a process is similar to carbonate weathering and dissolution which would have otherwise occurred naturally, but over many millennia. Relative to atmospheric release or direct ocean $CO_2$ injection, this method would greatly expand the capacity of the ocean to store anthropogenic carbon while minimizing environmental impacts of this carbon on ocean biota. This carbonate-dissolution technique may be more cost-effective and less environmentally harmful, and than previously proposed $CO_2$ capture and sequestration techniques.

## Introduction

The continued large-scale anthropogenic emission of carbon dioxide into the atmosphere may produce climate change with adverse impacts on the environment and economy. Methods proposed to avert such climate change include sequestering fossil-fuel $CO_2$ in reservoirs that are isolated from the atmosphere (e.g., subterranean and deep ocean environments) [*Herzog and Drake,* 1996]. Injection of gaseous, liquid or solid $CO_2$ into the deep or mid-depth ocean suffers from the deficiency that much of the sequestered $CO_2$ will degas back to the atmosphere after several hundred years [*Hoffert et al.*, 1979; *Bacastow et al.*, 1997] (Figure 1).

Anthropogenic $CO_2$ released to the atmosphere will eventually be buried as carbonate sediments through a series of steps occurring on a broad range of time scales [*Sundquist et al.,* 1990; *Archer et al.,* 1997]. $CO_2$ emitted into the atmosphere equilibrates with the surface ocean on the scale of less than one year. This dissolved $CO_2$ is mixed from the surface to deep ocean on the scale of about 300 years. The acidity produced by the dissolved $CO_2$ is partially neutralized by the dissolution of carbonate minerals on the scale of ~6000 yr, allowing the ocean to absorb more $CO_2$ from the atmosphere. Ultimately, on the scale of $\sim 10^5$ yr, enhanced silicate-rock weathering will provide the cations needed to bury the anthropogenic $CO_2$ as carbonate sediments. Injection of $CO_2$ directly into the deep sea bypasses the surface-equilibration and mixing-to-deep-sea steps (Figure 1). The carbonate-dissolution method [*Rau and Caldeira,* 1999] largely bypasses these steps as well as the natural carbonate dissolution step by dissolving carbonate minerals at the site of $CO_2$ production. This carbonate dissolution would eventually occur naturally on land and in the sea, but over the course of many millennia [*Archer et al.,* 1997].



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## The Carbonate-Dissolution Method

The carbonate-dissolution method [*Rau and Caldeira,* 1999] of ocean $CO_2$ sequestration may be summarized as follows: $CO_2$-rich exhaust gases from fossil-fuel power plants, when dissolved in seawater in a reactor vessel at the power plant, would produce a carbonic acid solution. (We frame our discussion in terms of seawater, because of the large amounts of water needed for this process and the need to discharge the resulting waste water into the ocean, although any large volume water source could in principal be used.) This carbonic acid solution would be highly corrosive to calcite, aragonite, dolomite, limestone, and other carbonate-containing minerals, especially if the carbonate minerals had been crushed to increase reactive surface area. The overall net reaction for most of the reactants, using a calcium carbonate mineral as an example, would be

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2\,HCO_3^- . \qquad (1)$$

After some capture of $CO_2$ degassed from the reactor effluent, the relatively harmless solution of $Ca^{2+}$ and $HCO_3^-$ in seawater would be released back into the ocean, where it would be diluted by additional seawater. The increase in alkalinity from the $Ca^{2+}$ would tend to cause dissolved inorganic carbon to be present in the form of $HCO_3^-$, which cannot directly interact with the atmosphere. In this way, power plant $CO_2$ could be effectively stored in the oceans, largely as $HCO_3^-$.

Exhaust gases from fossil-fuel power plants typically have 0.15 atm partial pressure of $CO_2$ [*US DOE,* 1993], over 400 times that of ambient air. When dissolved and equilibrated in seawater this would produce a carbonic acid solution (Table 1, Column B) with a *p*H of 5.7 (or 4.8 if the gas was pressurized to produce a $CO_2$ partial pressure of 1 atm), highly corrosive to most common carbonate minerals. This carbonic acid solution would be brought into contact with carbonate

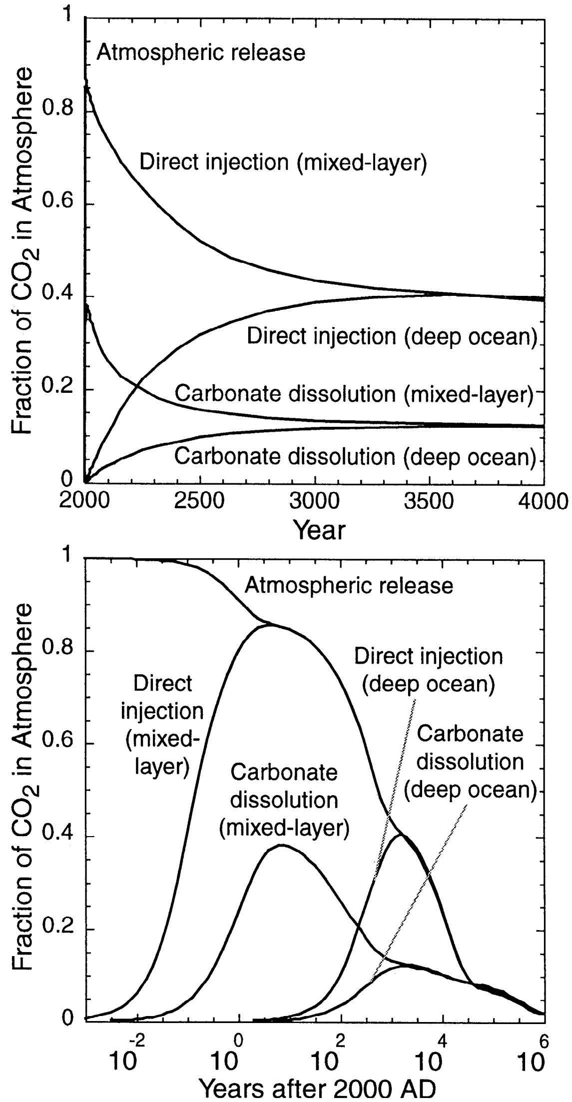


**Fig 1.** A comparison of the fraction of fossil-fuel $CO_2$ released that is in the atmosphere as a function of time under five different release scenarios. These scenarios are: atmospheric release, direct injection into the mixed-layer, release of carbonate-dissolution effluent into the mixed-layer, direct injection into the deep ocean, and release of carbonate-dissolution effluent into the deep-ocean, assuming background $CO_2$ concentrations stabilizing at 750 μatm as specified by the IPCC S750 scenario [*Enting et al.,* 1994]. The model was first run in inverse mode to compute the $CO_2$ emissions to the atmosphere that would yield the S750 atmospheric $CO_2$ concentrations. Supplementing these atmospheric emissions, all scenarios involve an additional release of fossil-fuel $CO_2$ equivalent to that present in the pre-industrial atmospheric content. Top panel has a linear horizontal axis; bottom panel is on a log scale.

minerals such as calcium carbonate (e.g., limestone), which could be crushed to increase reactive surface area. Calcium carbonate dissolution rates [*Plummer and Wigley,* 1976; *Arakaki and Mucci,* 1995] would be on the order of $2 \times 10^{-6}$ mmol $s^{-1}$ per $cm^2$ of reactive carbonate mineral surface area. If spherical carbonate particles of radius 1 cm are assumed, it would be necessary to present 100 tonnes of carbonate in a reactor volume of 45 $m^3$ to the incoming gas stream to sequester of 1 tonne $CO_2$ $day^{-1}$ [*Rau and Caldeira,* 1999]. This volume is likely to be an overestimate because the surface area per unit mass of crushed natural carbonate can be several orders of magnitude higher than that of uniform spherical particles [*Walter and Morse,* 1984]. Seawater in equilibrium with calcite at a $pCO_2$ of 0.15 atm will contain 20 mmol $kg^{-1}$ of total dissolved inorganic carbon, ~10 times that of typical surface seawater (Table 1, Column C); ~6.2 mmol $kg^{-1}$ will have been derived from the dissolution of calcite, and 11.6 mmol $kg^{-1}$ from fossil fuel combustion.

Surface ocean waters are already supersaturated with respect to calcite, but precipitation is kinetically impeded, apparently due to the presence of certain naturally-occurring ions in seawater [*Morse and Mackenzie,* 1990]. Therefore, some $CO_2$ could be degassed and recaptured without reprecipitating calcite; this recaptured $CO_2$ could be cycled back into the carbonate dissolution reactor, and the remaining solution could be discharged into the ocean with a calcite saturation state typical of surface seawater (Table 1, Column D). After this initial degassing, the solution would contain ~7.6 mmol fossil-fuel C per kg of seawater. At this concentration, a minimum of ~$1.1 \times 10^4$ tonne $H_2O$ $day^{-1}$ would be needed to discharge 1 tonne of fossil-fuel-derived C $day^{-1}$. This is an absolute minimum water requirement because the rate of carbonate dissolution will decline as saturation is approached [*Plummer and Wigley,* 1976]. Release of undersaturated water would require more water per tonne C sequestered.

When this solution is released from the reactor ($pCO_2 = 3.5 \times 10^4$ μatm; Table 1, Column D) the solution's elevated aqueous $CO_2$ concentration would result in degassing of $CO_2$ to the atmosphere and carbonate precipitation. However, if the outflow solution is diluted with seawater, 1 part to 100, and the diluted solution (Table 1, Column E) brought into equilibrium with the atmosphere, the calcite saturation state would increase by only ~10% (Table 1, Column F), an amount unlikely to initiate calcite precipitation. After equilibration with the atmosphere, ~0.66 mol of fossil-fuel C would be stored in the ocean for each mol of calcite dissolved. Actual efficiency could be between ~0.66 and ~1.22 (Table 1, Columns E and F), because some of this solution could enter the deep ocean without equilibrating with the atmosphere. Furthermore, engineering approaches could be adopted to place the solution in the deep sea, or to favor deep-sea mixing over atmospheric exchange. Nevertheless, using 0.66 as the ratio of $CO_2$ sequestered to calcite dissolved yields a demand of at least $1.7 \times 10^4$ tonne $H_2O$ per tonne C permanently sequestered. By comparison we note that coal-fired power plants consume roughly 800 tonne $H_2O$ per tonne coal burned [*Singer,* 1991] or ~1500 tonne $H_2O$ per tonne C released as $CO_2$. Thus, reuse of this water alone could be sufficient to permanently sequester up to 9 % of the fossil fuel $CO_2$ produced at the power plant. This is significant, considering that the Kyoto Protocol to the UN Framework Convention on Climate Change calls for Annex I countries to reduce emissions ~5% below nominal 1990 values [*Kyoto Protocol,* 1997].

## Geochemical Model and Results

To study the geochemical implications of the carbonate-dissolution method of ocean $CO_2$ sequestration, we performed several simulations using a schematic model of ocean chemistry and transport [*Caldeira and Rampino,* 1993], based on a three-box ocean model [*Toggweiler and*

**Table 1.** Chemistry calculation for the carbonate-dissolution method.

| | (A) initial seawater in equilibrium with atmosphere | (B) in equilibrium with 0.15 atm $CO_2$ | (C) in equilibrium with 0.15 atm $CO_2$ and calcite | (D) degassed to seawater $\Omega_{Calcite}$ | (E) diluted with 100 parts seawater | (F) degassed to equilibrium with atmosphere |
|---|---|---|---|---|---|---|
| $pCO_2$ (μatm) | 350 | 150000 | 150000 | 35339 | 415 | 350 |
| $\Sigma$Alk (μeq $kg^{-1}$) | 2314 | 2314 | 14808 | 14808 | 2438 | 2438 |
| $\Sigma CO_2$ (μmol $kg^{-1}$) | 2047 | 7459 | 19921 | 15893 | 2184 | 2149 |
| $CO_2$(aq) (μmol $kg^{-1}$) | 12 | 5143 | 5143 | 1212 | 14 | 12 |
| $HCO_3^-$ (μmol $kg^{-1}$) | 1844 | 2315 | 14749 | 14563 | 1983 | 1928 |
| $CO_3^{2-}$ (μmol $kg^{-1}$) | 191 | 1 | 29 | 118 | 187 | 209 |
| $Ca^{2+}$ (mmol $kg^{-1}$) | 10.12 | 10.12 | 16.37 | 16.37 | 10.18 | 10.18 |
| $\Omega_{Calcite}$ | 4.14 | 0.02 | 1.00 | 4.14 | 4.14 | 4.56 |
| *p*H | 8.22 | 5.69 | 6.50 | 7.12 | 8.18 | 8.24 |
| $ffCO_2/CaCO_3$ dissolved | | | 1.86 | 1.22 | 1.22 | 0.66 |

Carbonate chemistry calculation as described in *Takahashi et al.* [1982] and *Peng et al.* [1987]. Seawater in equilibrium with the atmospheric $pCO_2$ (A) becomes highly unsaturated with respect to calcite when it is brought into equilibrium with the 0.15 atm $pCO_2$ typical of power-plant waste gases (B). This solution can be used to dissolve carbonate minerals, however the resulting solution has a very high partial pressure of $CO_2$ (C). Some of this $CO_2$ can be degassed and recycled back into the carbonate dissolution reactor, bringing the calcite saturation state of the waste water up to that typical of surface seawater (D). To prevent calcite precipitation upon further degassing, the solution is diluted with additional seawater (E), e.g. by release into the open ocean. After further degassing and equilibration with the atmosphere (F), ~0.66 mol of fossil-fuel $CO_2$ ($ffCO_2$) has been permanently sequestered away from the atmosphere for each mol of $CaCO_3$ dissolved.

*Sarmiento,* 1985] and a carbonate-silicate cycle model [*Berner,* 1990]. The ocean/carbonate-silicate-cycle model used here [*Caldeira and Rampino,* 1993] has deep ocean, surface ocean, and polar outcrop reservoirs of carbon and alkalinity, and an atmospheric carbon reservoir. Relevant processes considered include the weathering of carbonate and silicate minerals on land, advective, mixing and biological transport among high and low latitude, and deep ocean reservoirs, the production of shallow-water carbonate minerals, and the production and dissolution of biogenic organic carbon and carbonate minerals in the ocean, and air-sea gas exchange of carbon. The model configuration used here differs from that of *Caldeira and Rampino* [1993] in that ocean temperatures, and mixing and advective fluxes were the same as those used by *Toggweiler and Sarmiento* [1985], and ocean carbonate chemistry is calculated as described by *Takahashi et al.* [1982] and *Peng et al.* [1987].

This model qualitatively reproduces the results for atmospheric $CO_2$ releases obtained from more complicated models [e.g., *Archer et al.,* 1997]. Figure 1 shows the result of model simulations for an injection of $CO_2$ equal to the pre-industrial atmospheric content (= 4.93 x $10^{16}$ mol), with the $CO_2$ released into the atmosphere, directly injected into the ocean mixed-layer and deep ocean, and the carbonate-dissolution discharge (Table 1, Column D) released into the ocean mixed-layer and deep ocean, assuming a background $CO_2$ emissions scenario stabilizing atmospheric $CO_2$ at 750 μatm according to the IPCC S750 scenario [*Enting et al.,* 1994]. A millennium after the $CO_2$ is released, there is little difference whether the $CO_2$ was initially released into the atmosphere or deep ocean. However, over this time frame, the carbonate-dissolution method is more than three times as effective at attenuating an increase in atmospheric $CO_2$ as either direct atmospheric or deep-ocean release (Figure 1).

To investigate deep-ocean *p*H changes and long-term effectiveness as a function of amount of $CO_2$ sequestered in the ocean, we ran the model from an initial pre-industrial state, adding between 0 and $10^4$ Gt fossil-fuel C (1 Gt = $10^{12}$ kg) into the deep-ocean as $CO_2$ or as a component of the solution generated by the carbonate-dissolution process with the composition described in Table 1, Column D. It is anticipated that changes in ocean *p*H could adversely impact marine biota [*Caulfield et al.,* 1997; *Takeuchi et al.,* 1997]. These acceptability of these impacts are likely to limit the capacity of the ocean for carbon sequestration. Our results (Figure 2) indicate that, per tonne fossil-fuel C released, either direct injection or atmospheric release of $CO_2$ would affect ocean *p*H about six times as much as would the carbonate-dissolution method. Furthermore, 1000 years after release of anthropogenic $CO_2$, either direct injection or atmospheric release would leave at least 2.3 times and up to 5 times more $CO_2$ in the atmosphere than would the carbonate-dissolution method, depending on the amount of $CO_2$ released (Figure 2).

## Discussion and Conclusions

There are many tradeoffs to be analyzed in the design of an economically optimal carbonate-dissolution reactor [*Rau and Caldeira,* 1999]. Up to 1.5 mole of carbonate mineral must be dissolved for each mole of anthropogenic $CO_2$ permanently sequestered in the ocean. This would require a substantial infrastructure to mine, transport, crush and dissolve these minerals, as well as substantial pumping of seawater for a large-scale operation. These considerations suggested that coastally located power plants proximate to carbonate mineral sources would be favored. Factors to be considered in reactor design include water flow rate, gas flow rate, particle size, pressure, temperature, hydrodynamic conditions, purity of reactants, gas-water contact area, and so on. Consideration all of the preceding factors has led to preliminary cost estimates as low as \$68 per tonne C sequestered [*Rau and Caldeira,* 1999], as compared to > \$300 per tonne C estimated for deep-sea $CO_2$ injection [*Fujioka et al.,* 1997]. The carbonate-dissolution method will not remove all the $CO_2$ from a gas stream, because excess $CO_2$ is required to produce a solution that is corrosive to carbonate minerals. If complete $CO_2$ removal is required, the carbonate-dissolution method could be used in conjunction with other techniques of $CO_2$ sequestration.

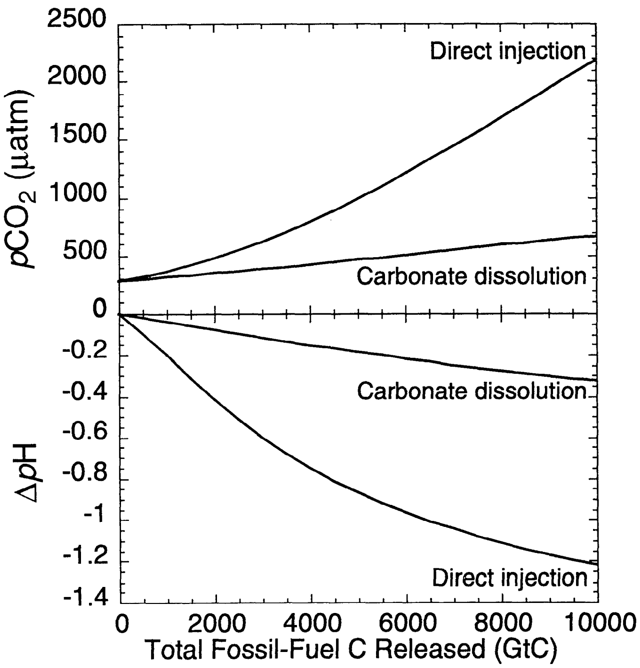


**Fig. 2.** Comparison of the effects of direct $CO_2$ injection and the carbonate-dissolution technique, both released into the deep-ocean, on atmospheric $CO_2$ content (top panel) and deep-ocean *p*H (bottom panel) 1000 years after injection. If the ocean's anthropogenic carbon capacity were determined by the amount of $CO_2$ that would shift ocean *p*H by 0.3 units, then the carbonate-dissolution technique would increase the ocean's capacity by roughly a factor of six. With the direct-injection method, for large amounts of anthropogenic $CO_2$ released, over 45 % of the injected $CO_2$ is in the atmosphere after 1000 yr. With the carbonate-dissolution method, less than 15 % of the initially released $CO_2$ degasses to the atmosphere.

In summary, the carbonate-dissolution method of ocean $CO_2$ disposal is geochemically and environmentally advantageous because the dissolution of carbonate minerals neutralizes $CO_2$-acidity, and largely converts $CO_2$ to a form that does not exchange with the atmosphere. Because the waste water generated by the carbonate-dissolution method would be relatively benign and can be released into shallow subsurface waters, this method largely obviates the need for large amounts of energy in separating and injecting $CO_2$ deeply into the ocean. Further experimental work is needed to test whether this method can be applied economically on a large scale. While no single approach is likely to solve the entire $CO_2$ problem, the carbonate-dissolution technique for sequestering fossil-fuel carbon could contribute significantly to global $CO_2$ mitigation.

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K. Caldeira, DOE Center for Research on Ocean Carbon Sequestration, Lawrence Livermore National Laboratory, 7000 East Ave., L–103, Livermore, CA 94550 USA. (e-mail: kenc@llnl.gov)

G.H. Rau, Institute of Marine Sciences, University of California, Santa Cruz, CA 95064 USA.

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